Insect Sex Pheromones: Importance and Determination of Half-life in Evaluating Formulations

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ABSTRACT

A minimum rate of release of sex pheromone (R) is needed to assure adequate control of male insects by the air permeation technique. For formulations that emit pheromones at a rate proportional to the amount remaining, a mathematical relationship exists that relates the minimum release rate that will provide control, R; the period of control per application, t; the application level of the pheromone, M_0; and the half-life of the formulation, $t_{\frac{1}{2}}$: $M_0 = Re^{kt}/k$, where $k = (ln2)/t_{\frac{1}{2}}$ and e is the base of natural logarithms. A plot of M_0 versus $t_{\frac{1}{2}}$ for a given R and t has a minimum. Thus, pheromone useage will be minimized when the half-life is optimized for the desired period of control.

The equations presented in this paper may be used to calculate the trade off between the number of applications versus the amount of pheromone applied for a given formulation or to evaluate the relative suitability of a series of formulations for a given field situation in terms of the half-lives of the formulations. Because $t_{\frac{1}{2}}$ is such an important parameter, experimental factors important in its determination are discussed.

KEYWORDS: insect sex pheromones, insect sex attractants, sex pheromone formulations, sex attractant formulations

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INSECT SEX PHEROMONES: IMPORTANCE AND DETERMINATION OF HALF-LIFE IN EVALUATING FORMULATIONS

By L. M. McDonough[1]

INTRODUCTION

The structures of a variety of insect sex pheromones are now known, and methods of formulating them for use in insect control are actively being sought. Developing substrates for control by the air permeation technique is a difficult problem because of the small amounts to be used and their high volatility. The area to be controlled must be treated with pheromone in such a way that there is a more or less even distribution of evaporating pheromone throughout the control area (5).[2] Apparently, the ability of males to locate females is suppressed either because the olfactory sense of the insect becomes fatigued and unresponsive, or because the male is distracted from females by the greater number or greater potency of artificial sources of attractant.

The distribution of the pheromone required for the air permeation technique may be achieved by using widely spaced evaporators (4) or by broadcast spraying formulated pheromone (8). Although both methods are worth investigation, the latter method may be more practical. Materials worth considering as candidates for formulating sex pheromones for broadcast spraying include liquid rubber or other liquid plastic, powdered or granular rubber, Austin Science Associates polymer-coated diatomaceous earth, Pennwalt Corp. microcapsules, National Cash Register Co. microcapsules, Moleculon Research Corp. microcapsules, Albany International Conrel fibers, and ground Heath Chemical Corp. Hercon laminates. The objective in this publication is to present mathematical relationships that can be used to evaluate one type of these formulations.

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[2]Italic numbers in parentheses refer to Literature Cited, p. 13.

Formulations, prepared with all the cited substrates except the Conrel fibers, are expected to emit pheromones by a first-order process (2,3). A first-order evaporative process is one in which the rate of evaporation of a substance, in this case the pheromone, is proportional to the amount remaining. When this is the case, the following relationship holds (Appendix 1):

$$M_0 = Re^{kt}/k, \text{ and } k = \frac{ln2}{t_{\frac{1}{2}}} \tag{1}$$

In this equation, M_0 is the amount of pheromone applied; R is the minimum evaporation rate that will produce control; e is the base of natural logarithms; k (referred to as the rate constant) is a value that is defined by the half-life, $t_{\frac{1}{2}}$, provided by the formulation; and t is the period for which control will be achieved.

If one could deliver pheromone continuously to a field plot so that the pheromone lost by evaporation was precisely replaced, then the amount required for any period would be $M_0 = Rt$ regardless of the value of the half-life. In practice, there is a practical limit to the frequency of application. Once one decides upon the period between applications or the period for which control is to be achieved from one application, this period becomes t, and the amount to be applied will be given by equation 1.

It is instructive to construct a graph of $t_{\frac{1}{2}}$ versus M_0 for equation 1. This can be done once t is decided upon and R is known. Taking $t = 30$ days and $R = 0.16$ grams per hectare-day, I obtained the curve of figure 1. This curve exhibits two interesting features: (1) There is a minimum value of M_0 (at $t_{\frac{1}{2}} = 20.8$ days); and (2) as $t_{\frac{1}{2}}$ is decreased sufficiently, a region is reached where M_0 increases extremely fast with decreasing $t_{\frac{1}{2}}$. Similarly shaped curves would be obtained for other values of t and R.

The most desirable half-life for a formulated pheromone would be that which required the minimum value of M_0. The appropriate equations for the general case are (Appendix 2):

$$t_{\frac{1}{2}}^{*} = t \; ln2 \approx 0.7t \tag{2}$$

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$$\overset{*}{M_0} = eRt \tag{3}$$

Here $\overset{*}{t_{\frac{1}{2}}}$ is the value of $t_{\frac{1}{2}}$ that gives the minimum M_0, and $\overset{*}{M_0}$ is the value of the minimum M_0.

It is interesting to compare $\overset{*}{M_0}$ with the amount of pheromone required if a formulation emitted pheromone by a zero-order process. For a zero-order process, the rate of emission is constant and independent of the concentration. This would be ideal for minimizing the amount of pheromone required. The amount required for a zero-order process is simply Rt. Since the ratio of $\overset{*}{M_0}$ to the amount required for a zero-order process (eRt/Rt) is e, an optimum formulation that emits by a first-order process will require about 2.7 times as much pheromone as a formulation that emits by a zero-order process. (Although no formulation actually emits by a zero-order process, Conrel chopped fibers are claimed to approximate zero-order release.) An experimentally determined constant rate of evaporation could represent not a zero-order release, but a first-order release with a very long half-life. The rate of emission would not actually be constant but could appear to be so. Such a formulation will use more pheromone and not less than $\overset{*}{M_0}$ as shown by figure 1.

Although the most desirable $t_{\frac{1}{2}}$ for a formulation is $\overset{*}{t_{\frac{1}{2}}}$, this value may not always be achievable. With some pheromones, it may be difficult to achieve such a long half-life. Since figure 1 shows that M_0 increases slowly with decrease of $t_{\frac{1}{2}}$ in the vicinity of $\overset{*}{t_{\frac{1}{2}}}$, a compromise of a moderate increase in M_0 for a significantly shorter $t_{\frac{1}{2}}$ is possible. We desire a general equation that will define $t_{\frac{1}{2}}$ and M_0 at the point (on the general curve of which figure 1 is a specific example) at which M_0 values increase sharply with a decrease in $t_{\frac{1}{2}}$. The values for this point are (Appendix 3):

$$t_{\frac{1}{2}}^{\dagger} = 0.2\ t \tag{4}$$

$$M_0^{\dagger} - 3.5\ \overset{*}{M_0} \tag{5}$$

Thus, when the half-life is 0.2 of the period of control, the amount that must be applied is 3.5 times that required when the half-life is 0.7 of the period of control. Values of $t_{\frac{1}{2}}^{\dagger}$ will result in very large increases in M_0 for small decreases in $t_{\frac{1}{2}}$, and thus are unlikely to be practical.
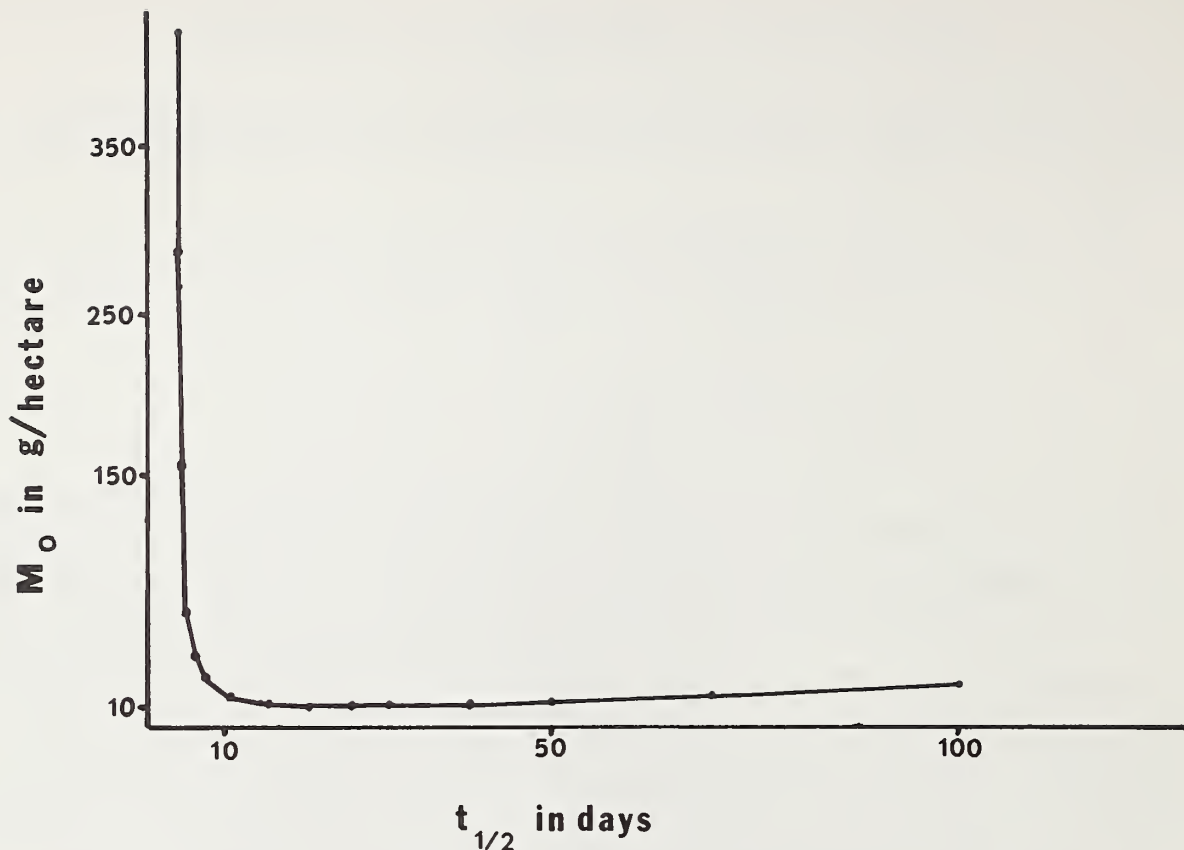
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Figure 1.--Relationship between the required application level of the
pheromone and the half-life of the formulated pheromone when the
minimum evaporation rate (R) to control the insect is 0.16 g/ha-
day, and the period of control is 30 days.

Equations 1 to 5, for determining the amount of pheromone to be applied,
are applicable for single applications. For more than one application, the
second and subsequent applications can be less because these will be applied
before the pheromone is exhausted. These subsequent applications would be made
when the rate of evaporation has decreased to the value R. The amount left will
be R/k, and the amount applied on the second and subsequent applications will be
decreased by the value R/k. The following examples will illustrate these points.
Suppose that one desired a 30-day period of control with one application, that a
formulation was available with $t_{\frac{1}{2}} = t_{\frac{1}{2}}^{*} = 20.8$ days, and that R was 0.05 g/ha-day;
then, $M_0^{*} = eRt = e(0.050)(30) = 4.08$ g/ha. Suppose, for a second case, that t
and R are the same as for case 1, but that $t_{\frac{1}{2}} = 2.1$ days. If one desires to
minimize the amount of pheromone used per application, then pheromone would be
applied every 3 days ($t = t_{\frac{1}{2}}^{*}/0.7 = 2.1/0.7 = 3.0$) and 10 applications would be

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required. The total amount of pheromone to be applied would then be:

$$M_0^* + 9(M_0^*-R/k) \quad , \quad k = \frac{ln2}{t_{\frac{1}{2}}} = \frac{ln2}{2.1} = 0.33$$

Therefore, the total is:

$$e(0.050)(3) + 9[e(0.050)(3) - (0.050/0.33)] = 2.71 \text{ g/ha}$$

Thus, this formulation would require 1.37 g less pheromone than for case 1, but nine more applications. Assume again the $t_{\frac{1}{2}}$ of the second case, but that one desires to minimize the number of applications. This can be done by using $t_{\frac{1}{2}}^{\dagger} = 0.2\ t$. Then $t = 2.1/0.2 = 10.5$ and three applications would be required. The amount of pheromone used would be:

$$M_0^{\dagger} + 2\ (M_0^{\dagger}-R/k) = (3.5)(e)(0.050)(10.5)$$
$$+ 2[(3.5)(e)(0.050)(10.5)$$
$$- (0.050)/0.33] = 14.7 \text{ g/ha}$$

This is a fairly large value and may be too large considering the expense of many pheromones. Decreasing the number of applications further (corresponding to $t_{\frac{1}{2}} < 0.2\ t$) will cause even larger increases in the amount needed to achieve a 30-day period of control; for example, two applications would require 42.6 g and one application would require 3,020 g of pheromone. Equation 1 could be used to calculate the total amount of pheromone to be used for more than 3 but less than 10 applications.

The last case to consider is the same as case 1 except that applications every 10 days might be more practical. How much pheromone could be saved for $t_{\frac{1}{2}} = 20.8$ days, if three applications instead of one are used? The total amount used would be:

$$M_0 + 2(M_0-R/k) \text{ and } k = \frac{ln2}{21} = 0.033$$

and the total would be:

$$Re^{kt}/k + 2(Re^{kt}/k-R/k) = (0.05)e^{(0.033)(10)}/0.033$$
$$+ 2[(0.050)e^{(0.033)(10)}/0.033$$
$$- (0.050/0.033)] = 3.29 \text{ g/ha}$$

The difference of $4.08 - 3.29 = 0.79$ g/ha of pheromone would be saved by making three applications instead of one.

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These examples illustrate that the equations presented in this section may be used to calculate the trade off between the number of applications versus the amount of pheromone used for a given formulation or to evaluate the relative suitability of a series of formulations for a given field situation in terms of the half-lives of the formulations.

These equations show that $t_{1/2}$ and R are two of the parameters that need to be evaluated to determine the suitability of formulations for a control program. These parameters can be evaluated from field data by determining the period of efficacy for a formulation applied at two different rates. This is most easily done by comparing pheromone trap catches in treated versus nontreated fields. This requires a decision on how large a trap catch can be tolerated. Generally, values of catches in treated fields as a percentage of nontreated between 1 and 5 percent are considered the largest that can be tolerated. If the formulation is applied at two rates, both high enough to give control, one would then monitor the traps until the catch increased to the percentage value previously decided on. The half-life is then calculated from:

$$t_{1/2} = \frac{(t_1 - t_2) \ln 2}{\ln(M_1/M_2)}$$

Here t_1 is the period of efficacy obtained when the lower application rate was used, and t_2 is the period of efficacy for the higher application rate. M_1 and M_2 are the lower and higher application rates, respectively. Once $t_{1/2}$ is known, k and then R can be calculated from equation 1. To assure the validity of this approach, evaporative release rate curves should be obtained in the laboratory for formulations to be tested in the field. Then, one can be sure that the evaporative release is a first-order process, or if complications in the release mechanism are present, knowledge of such complications may allow one to take these into account in the field tests.

DETERMINATION OF $t_{1/2}$ IN THE LABORATORY

Determination of $t_{1/2}$ by chemical analysis can be accomplished either by measuring the amount of pheromone remaining at intervals or by collecting and measuring the amount of emitted vapor per unit time at intervals. In the first instance, equation 6 would be applicable:

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$$lnM = lnM_0 - kt \qquad (6)$$

Here M is the amount remaining after time t, while M_0 and k are the same as be-
fore. Thus, a plot of lnM versus t would give a straight line with slope equal
to $-k$ and intercept equal to lnM_0. If the amount of emitted vapor per unit time
at intervals is determined, then equation 7 would be applicable:

$$lnkM = lnkM_0 - kt \qquad (7)$$

Here kM is the rate of emission at some instance and will change from instance
to instance. Since instantaneous rates cannot be measured, an actual measure-
ment will be an approximation, but very good approximations can be made. Then
a plot of $lnkM$ versus time will give a straight line with slope $-k$ just as in
equation 6 except that now the intercept will be $lnkM_0$ instead of lnM_0. An
interesting consequence of this equation is that if one knew beforehand that the
pheromone would have a first-order evaporative loss, then k could be determined
entirely from the initial rate of evaporation, which is equal to kM_0, because
M_0 would be known.

In principle, the rate constant k will be the same whether it is determined
by the amount of pheromone evaporating per unit time or by the amount remaining
if temperature and airflow are the same in each case. However, when the amount
of pheromone evaporating per unit time is determined, airflow could change be-
cause some workers have found it convenient to age the test samples under one
airflow and then place them in an apparatus with a higher airflow for collection
of the effluent. Because the effect of increased airflow is to increase k (de-
crease $t_{\frac{1}{2}}$), it is important to understand the effect the foregoing experimental
procedure would have on the data obtained.

Figure 2 is a plot of $ln(kM)$ (= ln release rate) versus time. Line A rep-
resents the release rate for a sample exposed to one condition of airflow such
that $t_{\frac{1}{2}}$ = 8 days ($k = 3.61 \times 10^{-3}/h$). Line B represents the release rate that
the same sample would have if it were continuously in a collection device with
a higher airflow rate such that $t_{\frac{1}{2}}$ = 2 days ($k = 1.44 \times 10^{-2}/h$). The question
then is what sort of data will be obtained when the sample is aged at the condi-
tions that produce loss curve A and then placed periodically, for short intervals,
in the collection apparatus at the conditions that produce loss curve B?

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If the sample is in the collection apparatus at time zero, the release rate will be equal to the value at the intercept of line B, 2.8 µg/h. The initial amount is:

$$k_B M_0 / k_B = 2.8 \text{ µg/h} \div 1.44 \times 10^{-2}/\text{h} = 194 \text{ µg}$$

After 2 days of aging at the conditions for line A, the amount remaining will be:

$$M = M_0 e^{-kt} = 194 \ e^{-(3.6 \times 10^{-3}/\text{h})(48 \text{ h})} = 163 \text{ µg}$$

After these 2 days, when the sample is again placed at conditions for line B, the evaporation rate will be:

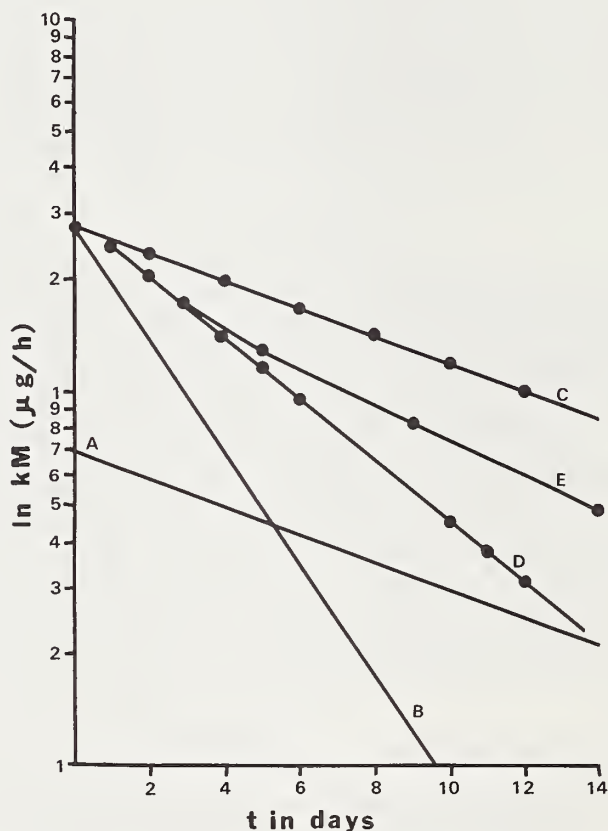$$k_B M = (1.44 \times 10^{-2}/\text{h})(163 \text{ µg}) = 2.35 \text{ µg/h}$$

Figure 2.--Changes in observed emission curves as caused by changes in technique of measurement: A, $t_{\frac{1}{2}}$ = 8 days; B, $t_{\frac{1}{2}}$ = 2 days. C, D, and E: These lines were constructed by considering a sample of evaporating pheromone to be exposed alternately for different periods to to conditions producing lines A and B.

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By proceeding in this way, I obtained the points that define line C, the line that would be obtained by the experimental procedure under consideration. The "experimentally" determined line, C, has the same slope as line A but the intercept of line B. If k were then determined from the slope of line C, its value would correspond to the k for the evaporation conditions of line A. This procedure, therefore, produces the k for aging for the conditions for line A as long as the time the sample is exposed to the conditions of line B is sufficiently small as compared with the time it is exposed to the conditions of line A.

Furthermore, if the time the sample is exposed to the conditions for line B is large enough to produce a detectable effect on the slope, a straight line with slope between those of lines A and B will be produced--providing the evaporation rate is measured at regular intervals. Thus, line D was calculated by assuming 0.6 day at the line B conditions and 0.4 day at the line A conditions. However, if the rate is not measured at regular intervals, the line will not be straight. For example, line E was constructed by assuming 9.6 h at line B conditions measured after periods of 1, 2, 3, 5, 9 and 14 days at line A conditions. As the interval between measurements increased, the percentage of time at the line B conditions decreased, and the slope approached the slope of line A.

Finally, if the amount of evaporating pheromone is small and therefore difficult to analyze, one could simply leave the sample in the collection apparatus, collect the emitted pheromone each day, and plot ln of the amount collected each day versus time. Since the first-order relationship is linear, the use of this large time interval will not change the slope of the line; however, the intercept will be changed because the average evaporation per day does not occur at the end of each day. The intercept occurs sometime during the day (but not at the middle of the day). Thus, all the points plotted at the end of each day will be shifted to the right, and the result will be an intercept above kM_0. Furthermore, the sampling intervals must again be kept constant. If the interval is increased, the distance of the plotted point to the right of its true position will also increase, and curvature will again be falsely introduced into the plotted line.

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If one plots the logarithm of the amount of pheromone remaining versus time and does not obtain a straight line, one could strictly conclude that the evaporation was not first order. Nevertheless, a straight line may not be obtained when the principal evaporative process is first order. Various complications may obscure this fact. Often, if these complications are understood, they can be taken into account and the results can still be analyzed with equations 1 to 5. In this section, factors that could lead to obscuring the existence of a first-order process or that could cause a misinterpretation of the rate of evaporation will be presented.

One possible complication is concurrent chemical degradation and evaporative loss. If the chemical degradation is, within experimental error, also first order, then the integral equation is:

$$lnM = lnM_0 - (k_1+k_2)t$$

where k_1 represents the rate constant for evaporative loss and k_2 represents the rate constant for chemical loss. If one measured the amount of pheromone remaining in such a case, the experimentally determined rate constant would be the sum of k_1 and k_2, which would lead to incorrect conclusions about the amount of pheromone evaporating. If one determined the amount evaporating per unit time (k_1M), the integral equation would become:

$$lnk_1M = lnk_1M_0 - (k_1+k_2)t$$

The slope of the line would still be $-(k_1+k_2)$; however, one could determine k_1 from the intercept, k_1M_0, by dividing by M_0, which would be known. Note that the intercept would have a value (k_1M_0) smaller than would have been predicted from the slope of the line ($k_1+k_2)M_0$. An alternate method would be to determine the amount remaining versus time and then collect all the vapors to see whether the amount emitted and the amount remaining accounted for the original amount (7).

Sometimes, simultaneous loss processes will give a more complicated loss curve, as, for example, when the evaporating material is in more than one physical state. Thus, in a complex formulation, a pheromone might simultaneously exist as (1) a pure liquid, (2) a dissolved liquid (for example, dissolved in a plastic), and (3) an adsorbed liquid (for example, adsorbed on the surface of a solid

material). The rate of evaporation from each state is then proportional to the concentration in that state alone and not to the total concentration of pheromone. The differential form of the equation for loss of pheromone then is:

$$-\frac{dM}{dt} = k_1 M_1 + k_2 M_2 + k_3 M_3 \text{ where } M_1 + M_2 + M_3 = M$$

(The subscripts indicate each individual physical state.) This equation cannot be converted to the integral form, but the general nature of a plot of lnM versus t can still be determined as shown in figure 3. Here most of the early loss of pheromone is the result of loss from the state that emits the fastest (assumed to be state 1). A plot of lnM versus time initially gives virtually a straight line with a slope somewhat similar to $-k_1$ (how similar depends on the actual values of $k_1 M_1$, $k_2 M_2$, and $k_3 M_3$). As the material in state 1 becomes depleted, the rate of loss from state 1 drops until most of the loss results from loss from state 2;

Figure 3.--General form of emission curve that results when pheromone exists in three different physical states, each with its own individaul emission rate. Emission of pheromone occurs concurrently from all three states: $k_1 M_1$, $k_2 M_2$, and $k_3 M_3$ represent rates of emission from fastest, next fastest, and slowest emitting states, respectively.

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then there will be a break in the line and a change to a slope determined mainly by $-k_2$. Finally, as state 2 becomes depleted, the slope will again change to the slope most similar to that for the slowest loss process; that is, evaporation from state 3. Such complex loss curves have been observed in studies of insecticide residues (6). A pheromone formulation that releases in such a fashion would be poor since it is very wasteful of pheromone, and its performance would be difficult to predict. However, when one is aware of this phenomenon, one can can sometimes devise methods of improving the formulation (7).

Another possibility is that some of the pheromone will be irreversibly bound in the formulation and only a portion will be available for evaporative emission. Such a situation would have no effect on the shape or slope of the curve if one were measuring the rate of emission. Figure 4 is an example. This plot shows the *ln* release rate versus time for a Pennwalt microcapsule formulation of the sex pheromone of the redbanded leafroller, *Argyrotaenia velutinana* (Walker) (1). The half-life of the released pheromone was 2.7 days. The authors reported that only 3.7 percent of the pheromone was released. One could determine
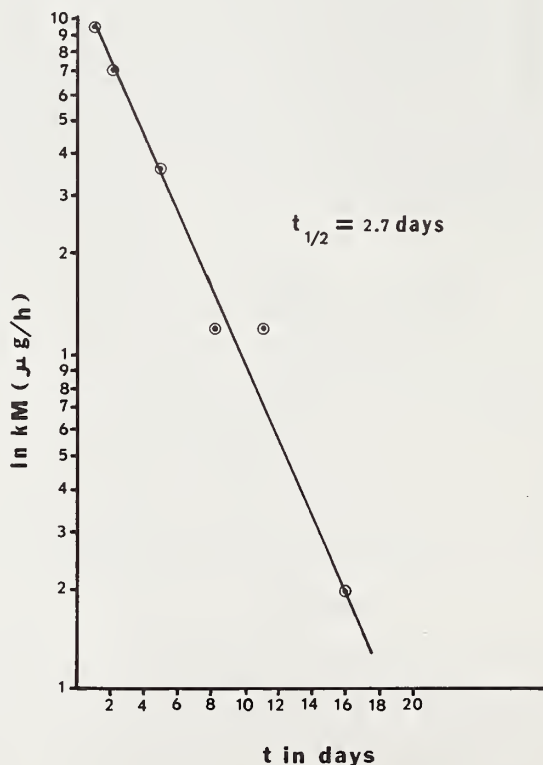

Figure 4.--Emission of sex pheromone of the redbanded leafroller from a microencapsulated formulation.

this latter fact by direct chemical analysis of the amount remaining after collecting the emitted vapors or by extrapolating the line of figure 4 to zero time and determining M_0 from kM_0/k. Obviously, when pheromone is irreversibly bound in the formulation, a loss curve obtained by determining the amount of pheromone remaining versus time would give a curved line from which determination of $t_{1/2}$ would not be possible.

The distribution of particle size is another factor that can affect the shape of a curve for first-order evaporative loss. The rate constant k is directly proportional to the surface area ($t_{1/2}$ is inversely proportional to the surface area). With two sets of spherical particles of equal total volume but unequal size, the ratio of their surface areas is inversely proportional to the ratio of their radii. Thus (Appendix 4):

$$\frac{k_2}{k_1} = \frac{{}^1 t_{1/2}}{{}^2 t_{1/2}} = \frac{r^1}{r_2}$$

where ${}^1 t_{1/2}$ is the half-life corresponding to particles of radius r_1, and ${}^2 t_{1/2}$ is the half-life corresponding to particles of radius r_2. Thus, too great a disparity in particle size will introduce an equivalent disparity in $t_{1/2}$ values and will cause curvature in an otherwise first-order plot.

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APPENDIX 1.--DERIVATION OF EQUATION 1

In an area that has been sprayed with a formulated sex pheromone, the amount
of pheromone remaining (M) will decrease with time as shown in figure 5. As M
decreases, the rate of pheromone emission will also decrease because $dM/dt = kM$.
If a sufficient amount of pheromone were applied, there would be a higher
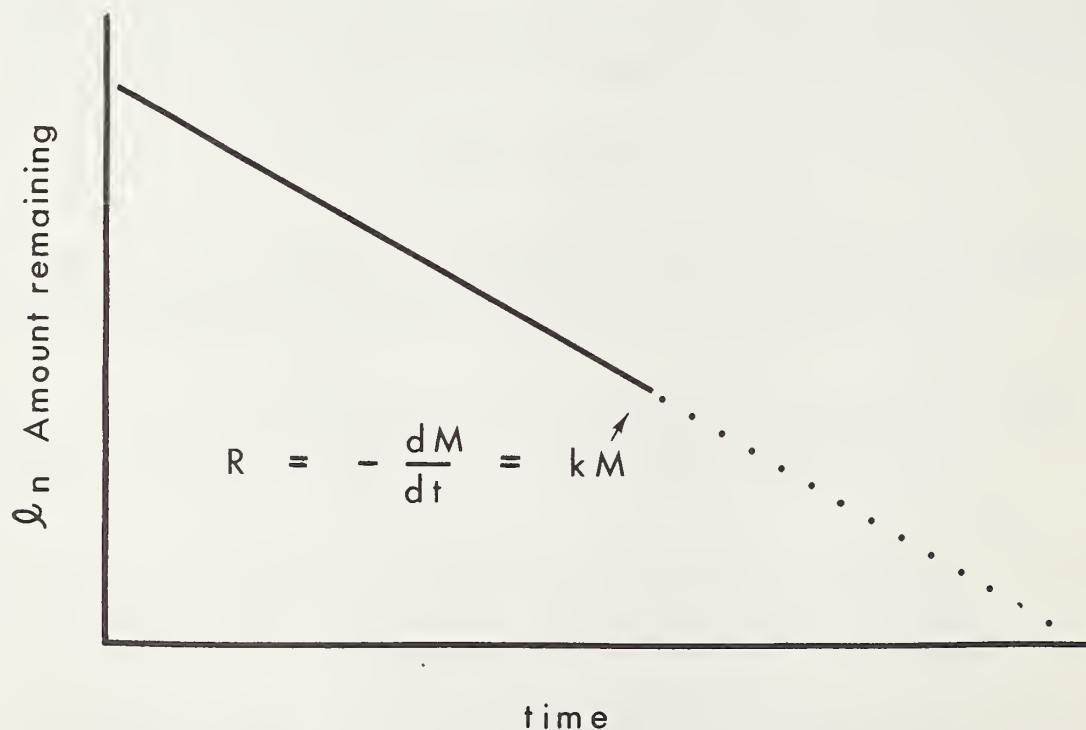initial emission rate than the minimum necessary for control. As the amount

$$R = -\frac{dM}{dt} = kM$$

Figure 5.--Plot of the logarithm of the amount of pheromone remaining
versus time for a first-order evaporation.

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remaining decreased, a point would be reached beyond which (dotted line in figure 5) the release rate would not provide control. This point would correspond to the minimum release rate necessary to effect control. This rate is denoted by R. For a particular formulation, $R = kM_m$ where M_m is a constant and is the M corresponding to the minimum amount of pheromone needed to achieve release rate R.

If the formulation is a variable, k will vary and the M corresponding to the minimum amount of pheromone needed to achieve release rate R will also vary because R is a constant. R/k may then be substituted for M in the integral form of the first-order equation:

$$ln(R/k) = lnM_0 - kt$$

which may be rearranged algebraically to:

$$M_0 = Re^{kt}/k \tag{1}$$

Here, e is the base of natural logarithms. In equation 1, R is a parameter characteristic of a given insect species, and since t is the period of time required for the release rate to decrease from its initial value to R, then t is the period of control obtained from one application of pheromone.

APPENDIX 2.--DERIVATION OF EQUATIONS 2 AND 3

$$M_0 = Re^{kt}/k \tag{1}$$

$$lnM_0 = ln(R/k) + kt$$

$$k = (ln2)/t_{\frac{1}{2}}$$

Therefore:

$$lnM_0 = \frac{t\ ln2}{t_{\frac{1}{2}}} + ln\left(\frac{Rt_{\frac{1}{2}}}{ln2}\right)$$

For simplicity, let:

$$M_0 = y$$

$$t_{\frac{1}{2}} = x$$

$$t\ ln2 = a$$

$$R/ln2 = b$$

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Then:

$$ln y = ax^{-1} + ln bx$$

$$y = e^{(ax^{-1}+ln bx)}$$

$$\frac{dy}{dx} = \left(e^{ax^{-1}+ln bx}\right) \left[\frac{d}{dx}(ax^{-1}+ln bx)\right]$$

$$= (1/x - ax^{-2})e^{(ax^{-1}+ln bx)}$$

For minimum y:

$$\frac{dy}{dx} = 0$$

Therefore:

$$\frac{1}{x} - \frac{a}{x^2} = 0$$

$$x - a = 0$$

$$x = a$$

Or:

$$t_{\frac{1}{2}} = t\, ln 2, \text{ denote } t_{\frac{1}{2}} \text{ by } t_{\frac{1}{2}}^{*} \tag{2}$$

$$ln M_0 = \frac{t\, ln 2}{t_{\frac{1}{2}}} + ln \left(\frac{R t_{\frac{1}{2}}}{ln 2}\right)$$

$$= \frac{t\, ln 2}{t\, ln 2} + ln \left(\frac{R t\, ln 2}{ln 2}\right)$$

$$= 1 + ln Rt$$

$$M_0 = eRt, \text{ denote } M_0 \text{ by } M_0^{*} \tag{3}$$

APPENDIX 3.--DERIVATION OF EQUATIONS 4 AND 5

$$M_0^{*} = eRt \tag{3}$$

$$M_0 = Re^{kt}/k \tag{1}$$

Divide equation 3 by equation 1

$$\frac{M_0^{*}}{M_0} = kte^{1-kt}$$

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Substituting $k = \dfrac{\ln 2}{t_{\frac{1}{2}}}$ (from equation 1) and $t = \dfrac{t_{\frac{1}{2}}^{*}}{\ln 2}$ (from equation 2), one obtains:

$$\frac{M_0^{*}}{M_0} = \frac{t_{\frac{1}{2}}^{*} e^{1 - t_{\frac{1}{2}}^{*}/t_{\frac{1}{2}}}}{t_{\frac{1}{2}}} \qquad (6)$$

Equation 6 can be used to calculate the increase in M_0/M_0^{*} with the decrease in $t_{\frac{1}{2}}$ as shown below:

$t_{\frac{1}{2}}^{*}/t_{\frac{1}{2}}$	M_0/M_0^{*}
1.0	1.00
1.5	1.10
2.0	1.36
2.5	1.79
3.0	2.46
3.5	3.48
4.0	5.02
5.0	10.92
6.0	24.74

For values of $t_{\frac{1}{2}}^{*}/t_{\frac{1}{2}}$ of from 1 to about 3.5, M_0/M_0^{*} is smaller than $t_{\frac{1}{2}}^{*}/t_{\frac{1}{2}}$, but for values greater than 3.5, the opposite holds. Therefore, $t_{\frac{1}{2}}^{*}/t_{\frac{1}{2}} \approx 3.5$ represents the point of the curve in figure 1 at which it breaks sharply upward. Decreasing $t_{\frac{1}{2}}$ below this point leads to very large increases in M_0. The $t_{\frac{1}{2}}$ for this point is designated $t_{\frac{1}{2}}^{\dagger}$. Then:

$$\frac{t_{\frac{1}{2}}^{*}}{t_{\frac{1}{2}}^{\dagger}} = 3.5$$

$$t_{\frac{1}{2}}^{\dagger} = \frac{t_{\frac{1}{2}}^{*}}{3.5} = \frac{t \ln 2}{3.5}$$

$$t_{\frac{1}{2}}^{\dagger} \approx 0.2t \qquad (4)$$

Also:

$$M_0^{\dagger} = 3.5 \, M_0^{*} \qquad (5)$$

where $M_0^{\dagger}$ is the M_0 corresponding to $t_{\frac{1}{2}}^{\dagger}$

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APPENDIX 4.--EFFECT OF SIZE OF SPHERICAL PARTICLES ON $t_{\frac{1}{2}}$

Let $V_1 = \frac{4}{3}\pi r_1^3$, volume of sphere of radius = r_1

$V_2 = \frac{4}{3}\pi r_2^3$, volume of sphere of radius = r_2

Let $V_2 < V_1$

Then:

$\frac{V_1}{V_2}$ = number of spheres of radius (= r_2) one could obtain from one sphere of radius (= r_1).

$A_1 = 4\pi r_1^2$, surface area of a sphere of radius = r_1.

$A_2 = 4\pi r_2^2$, surface area of a sphere of radius = r_2.

$\frac{V_1 A_2}{V_2}$ = total surface area of spheres of radius (= r_2) having a total volume of one sphere of radius r_1.

$\frac{V_1 A_2}{V_2 A_1}$ = ratio of the total surface area of spheres of radius (= r_2) to the surface area of one sphere of radius (= r_1).

$$ = \frac{4/3\ \pi r_1^3\ \cdot\ 4\pi r_2^2}{4/3\ \pi r_2^3\ \cdot\ 4\pi r_1^2} = \frac{r_1}{r_2} $$

Thus, the surface area ratio is equal to the inverse ratio of the corresponding radii. Since the rate constant is directly proportional to the surface area:

$$ \frac{k_2}{k_1} = \frac{^1 t_{\frac{1}{2}}}{^2 t_{\frac{1}{2}}} = \frac{r_1}{r_2} $$

where:

$^1 t_{\frac{1}{2}}$ = half-life of pheromone in sphere of radius r_1.

$^2 t_{\frac{1}{2}}$ = half-life of pheromone in spheres of radius (= r_2) and having a total volume equal to the volume of one sphere of radius (= r_1).

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M_0 The original or initial amount or mass of pheromone applied to a field for insect control. The usual units are grams per hectare (g/ha).

M The amount of pheromone present at any instance after the initial application. The usual units are grams per hectare (g/ha).

R The minimum evaporation rate of pheromone that would provide control of some area. The usual units are grams or milligrams per hectare-day (g or mg/ha-d).

e The base of natural logarithms. An irrational number whose approximate value is 2.71828. It has no units.

$t_{\frac{1}{2}}$ The half-life of a pheromone: The period of time for a pheromone to decrease to one-half of its original amount. For a first-order process, the half-life is independent of initial amount. Thus, if $t_{\frac{1}{2}}$ = 10 days, 1 g would decrease to 0.5 g in 10 days, 0.5 g would decrease to 0.25 g in another 10 days, and 0.25 g would decrease to 0.125 g in yet another 10 days, and so on. The usual units are days (d) or hours (h).

k The evaporative release constant is defined by $k = t_{\frac{1}{2}}^{-1} ln2$. When this constant is multiplied by M, the resultant value is the rate of evaporation. The units of k are reciprocal time, usually per hours (h^{-1}) or per days (d^{-1}).

t The period of time the pheromone application is efficacious. The usual units are days (d).

M_0^* The minimum amount of pheromone that must be applied to provide control for a given period of time. This minimum value will be sufficient only when the half-life is equal to $t_{\frac{1}{2}}^*$. The usual units are grams per hectare (g/ha).

$t_{\frac{1}{2}}^*$ When the half-life is equal to $t\ ln2$ ($\approx 0.7t$) then it is designated $t_{\frac{1}{2}}^*$. When the formulated pheromone has this value of half-life, then the amount of pheromone that must be applied to give control for the period t is at a minimum and is designated M_0^*.

$M_0^\dagger$ The value of M_0 necessary to provide control for a period t when $t_{\frac{1}{2}}$ = 0.2 t.

$t_{\frac{1}{2}}^\dagger$ The value of $t_{\frac{1}{2}}$ when $t_{\frac{1}{2}}$ = 0.2 t. For $t_{\frac{1}{2}}$ values shorter than $t_{\frac{1}{2}}^\dagger$, the values of M_0 are impractically large.